Establishing Absorbed Dose Thresholds for Nonlinearities in Water Calorimetry

- *heat transport and effects of radiolysis*

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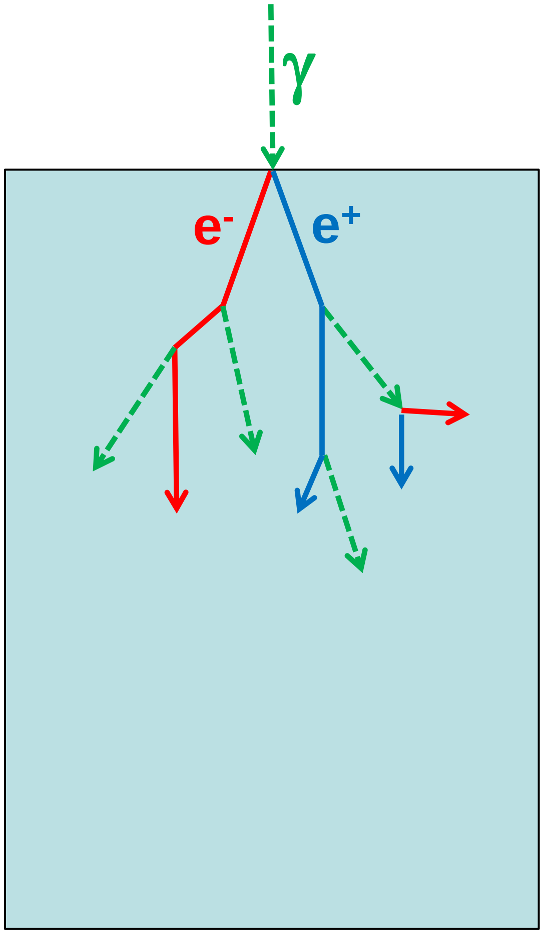
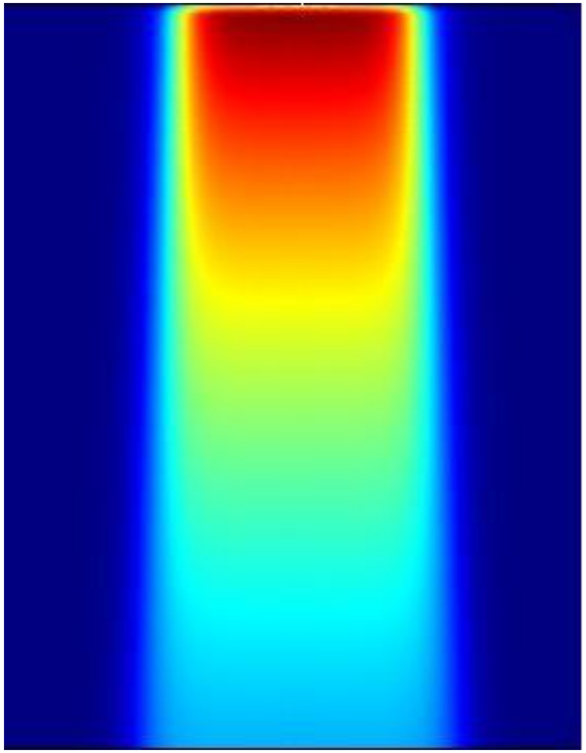
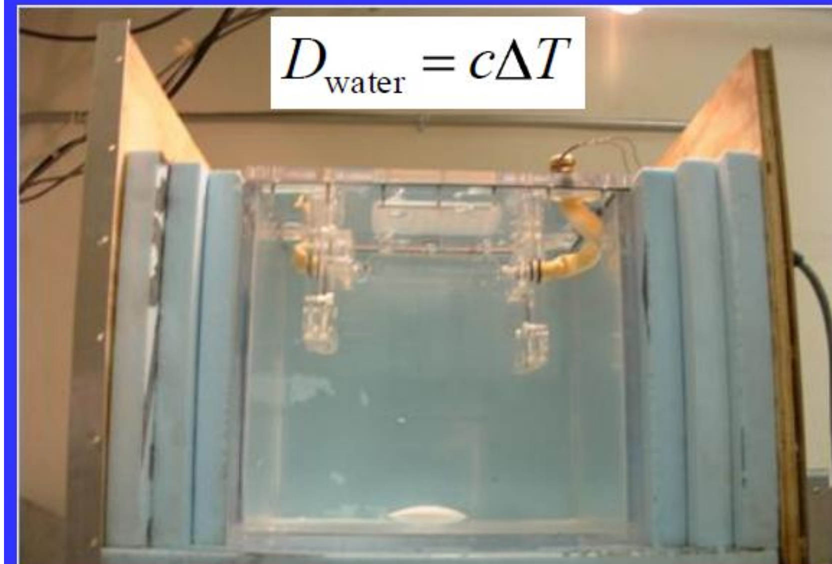
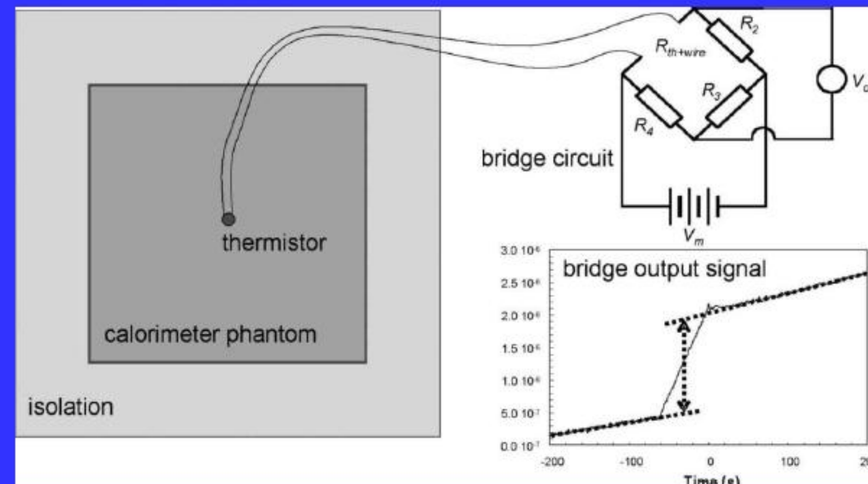
Dose is energy per unit mass: **J/kg = Gy**





The NIST Water Calorimeter

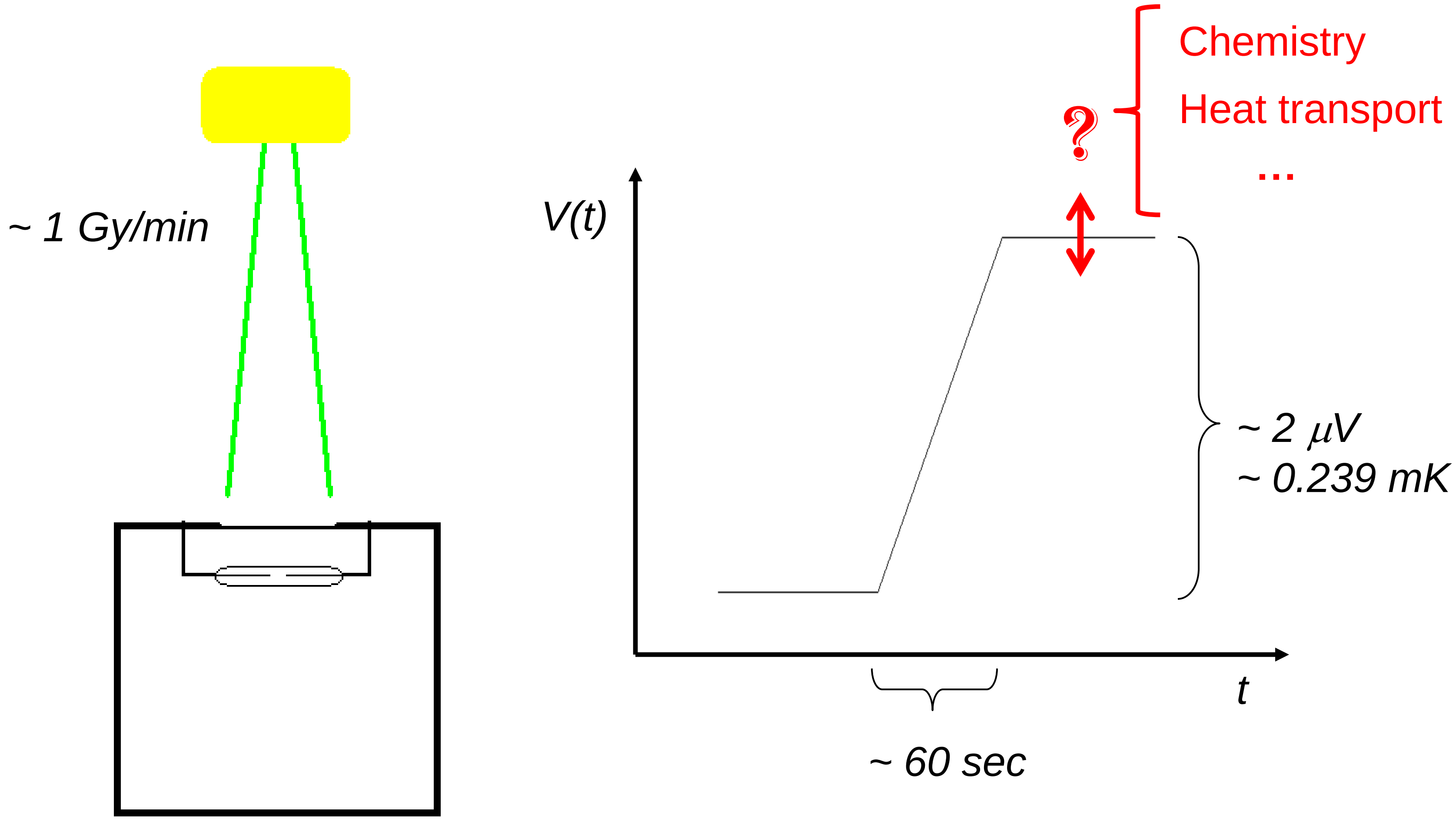




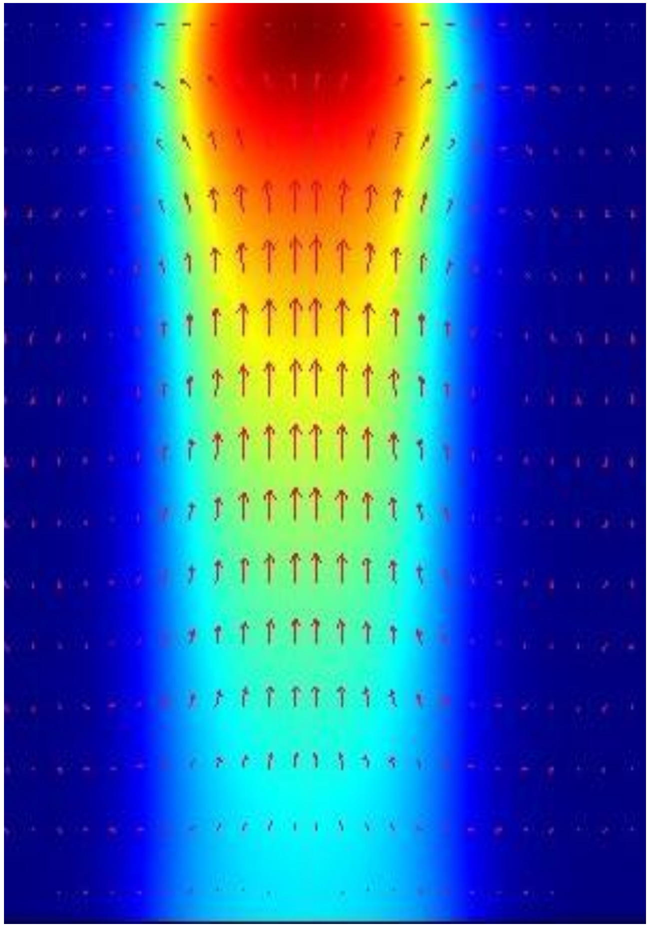
Vessel with thermistors

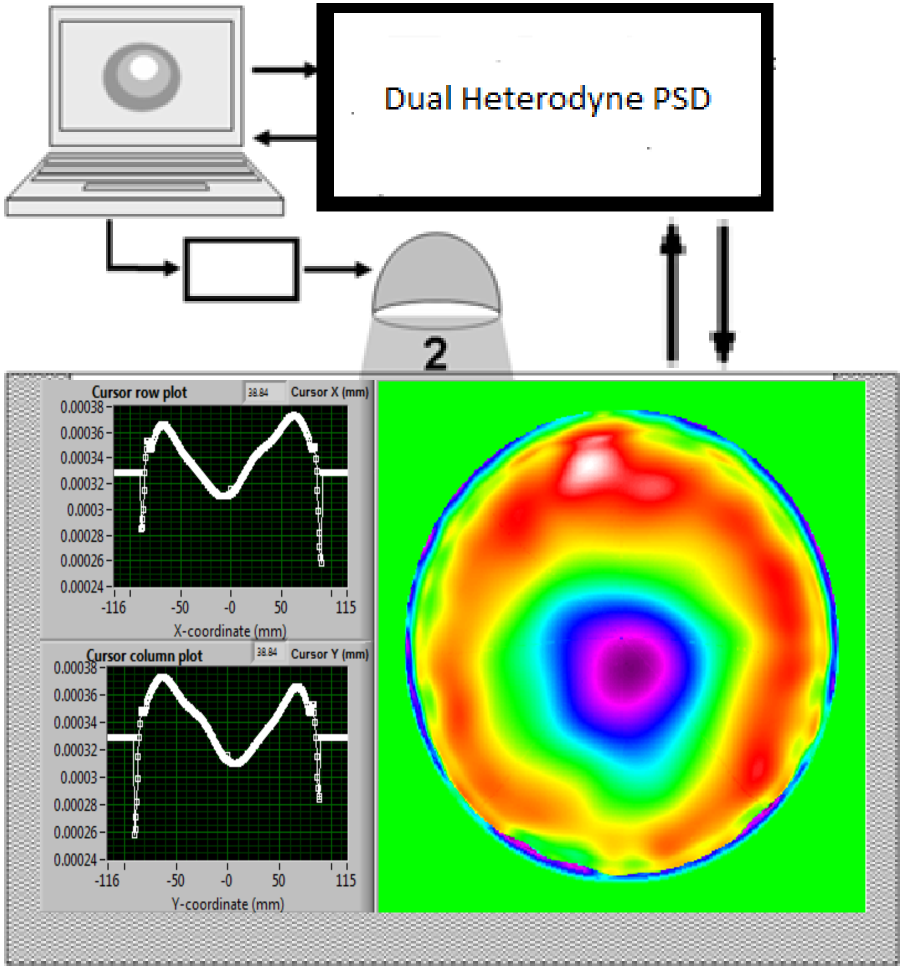
Vessel with an ion chamber

Experimental corrections



Natural convection in open phantom





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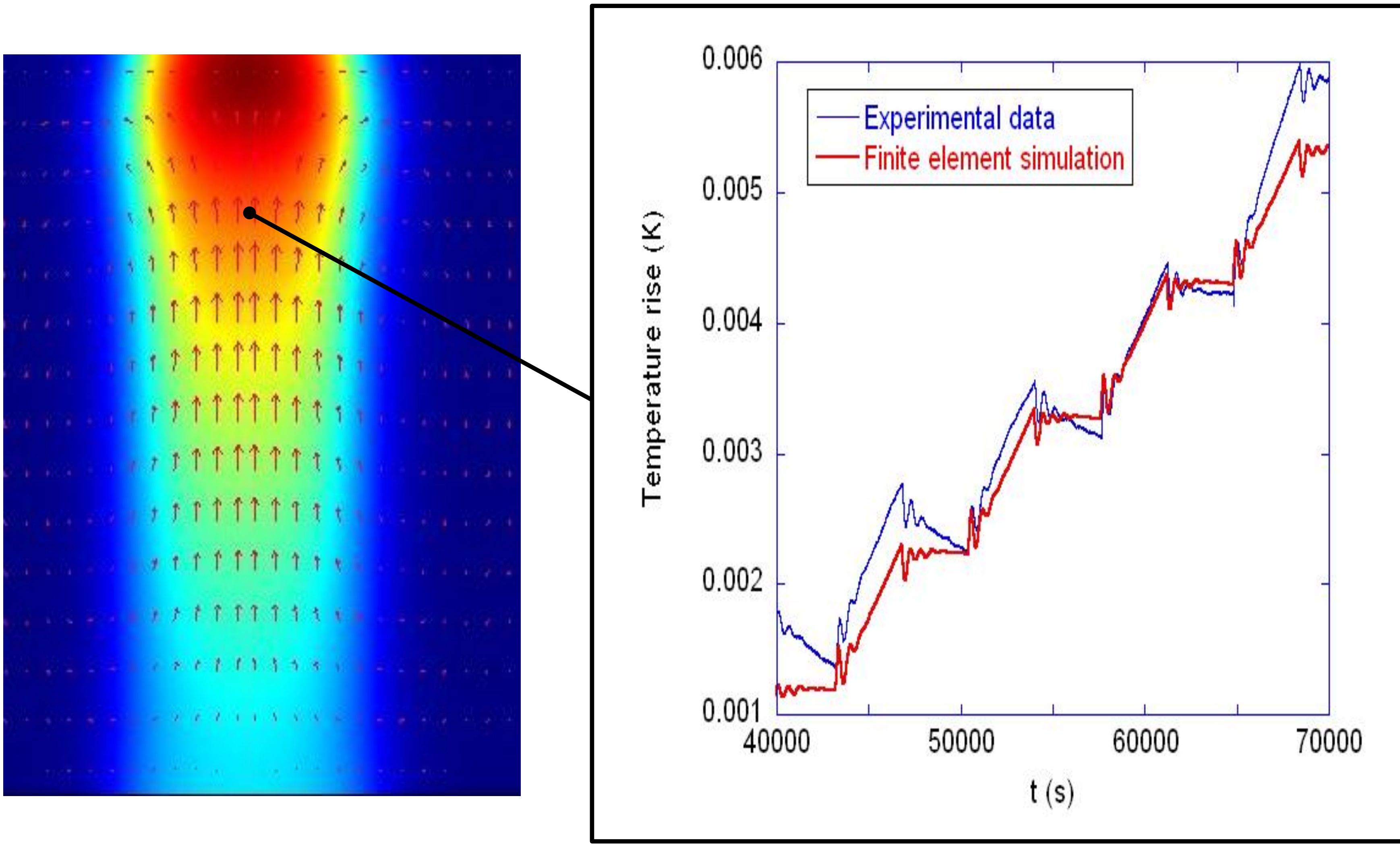
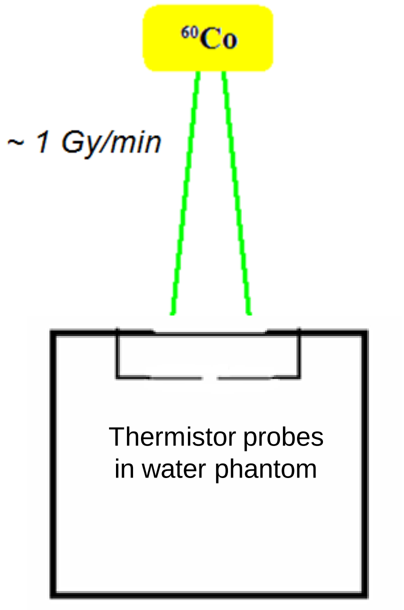
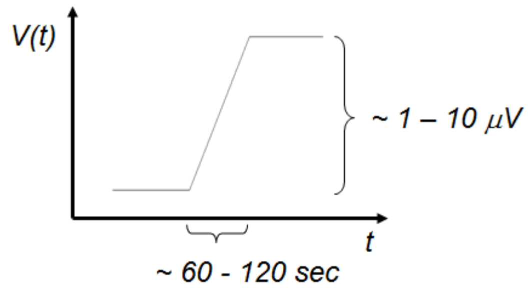


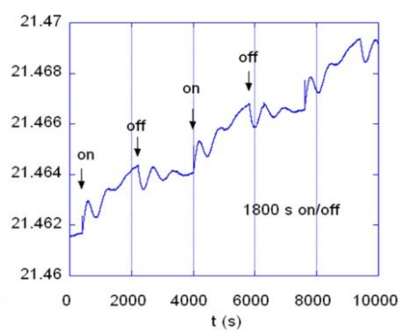
Heat Transport Effects





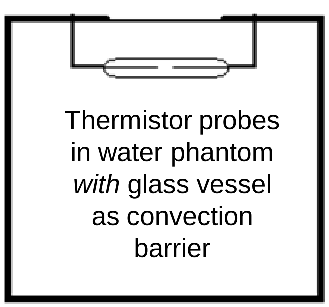
Ideal response

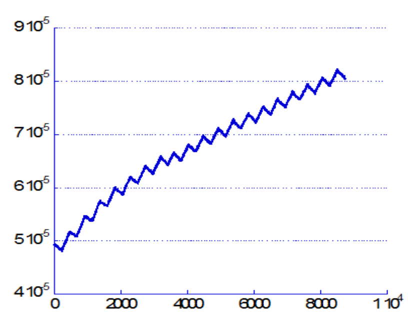
- Flat drift segments
- Linear rise when beam is on.
- Temperature rise ~ step height.



Conduction + Convection

- Severe distortions
- Convective oscillations
- Temperature rise very difficult to discern.



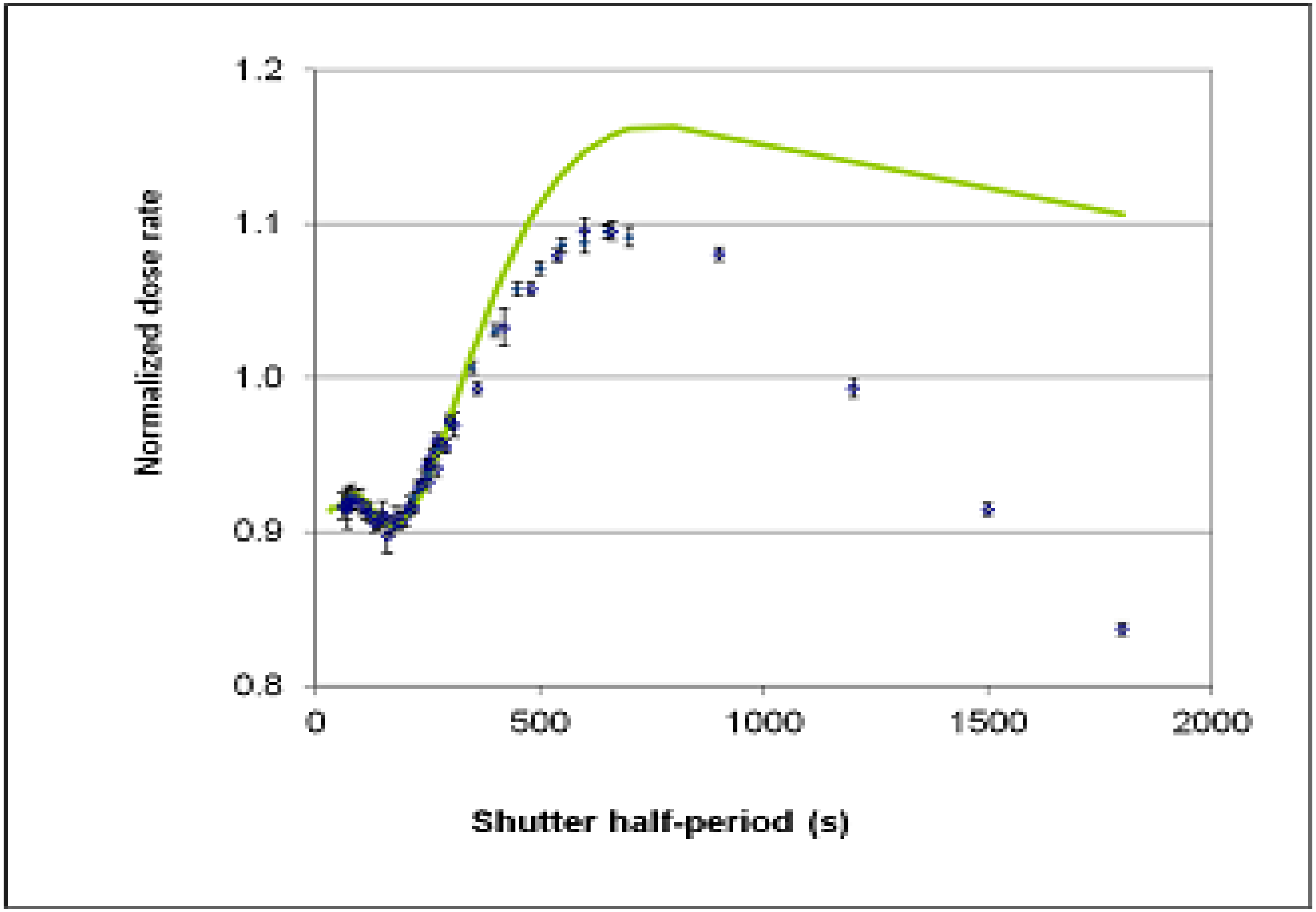


Conduction + Convection??

- Severe distortions
- No oscillations
- Temperature rise obtainable with corrections for convection *and/or* conduction.

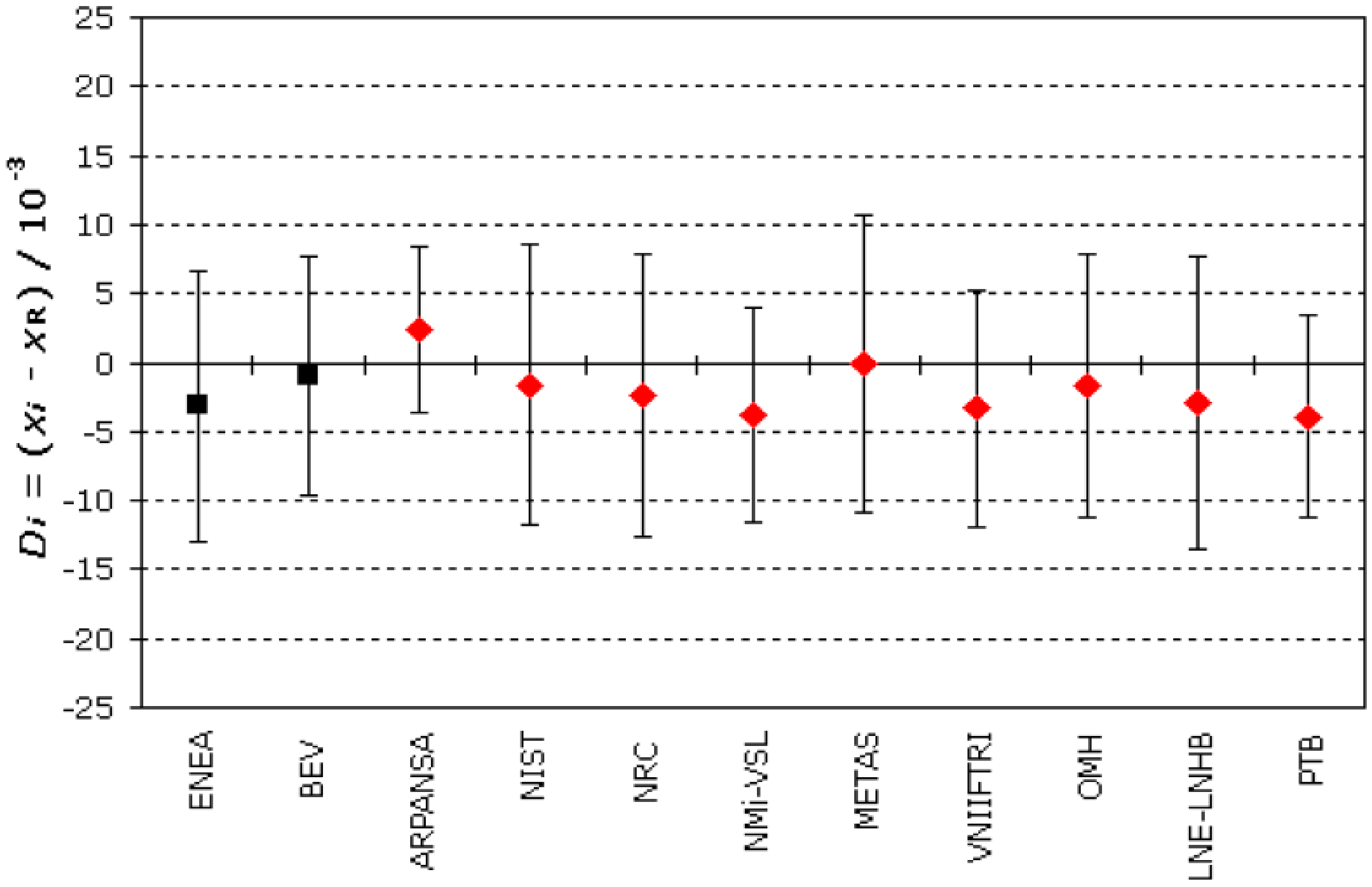
Evidence of convection at long shutter period

- conduction transfer function in green (COMSOL Heat Transfer Module)

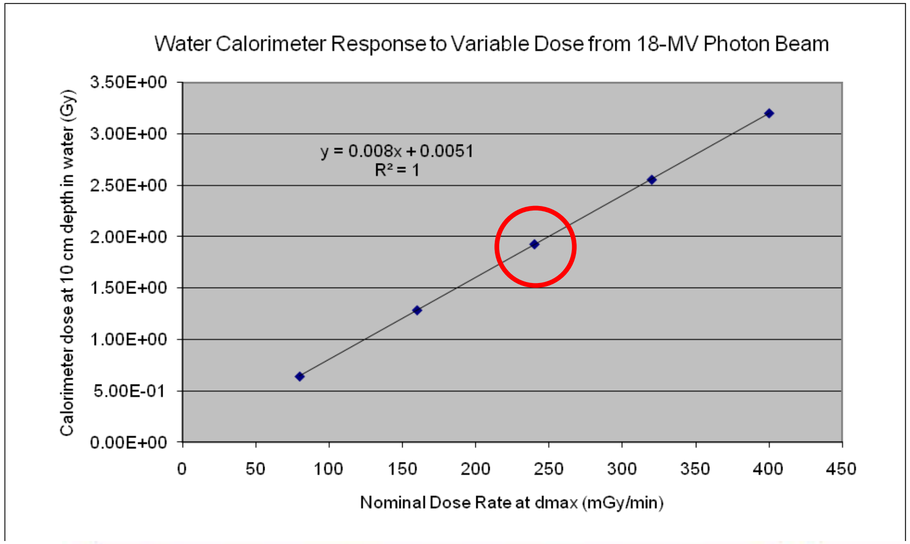


BIPM Intercomparison Program:

- Enables NMIs (like NIST) to declare calibration and measurement capabilities (CMCs)
- Key comparisons and database (http://kcdb.bipm.org)

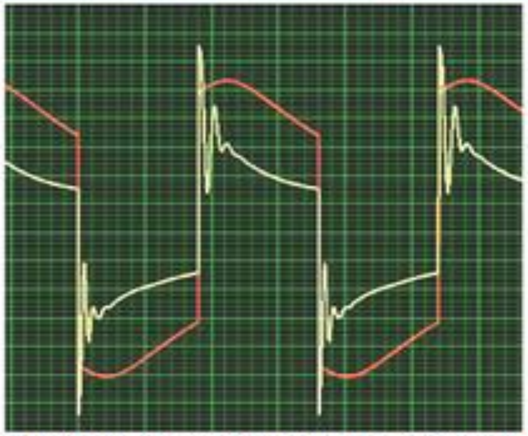


Dose-rate study: looking for nonlinearities

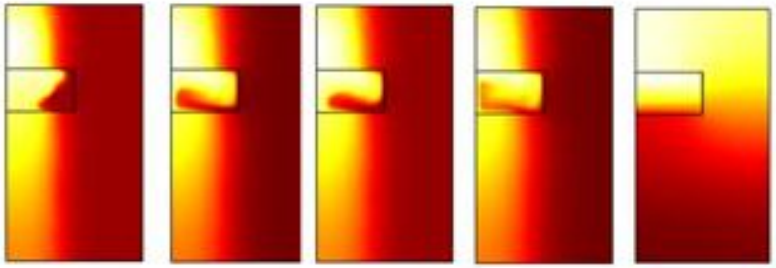


Test of calorimeter linearity over ~*5x* change in dose rate for a 18 MV beam.

- Clinac allows *5* discrete dose-rate levels (calibration runs were done at middle value).
- Slope of fit: (7.999e-3) ± (0.006e-3) Gy/MU
  Expected: 8 mGy/MU
- Suggests that convection is negligible (even at these elevated dose rates).



Time derivative of temperature waveform under periodic excitation, simulated with conduction only (red) and with convection enabled (yellow).



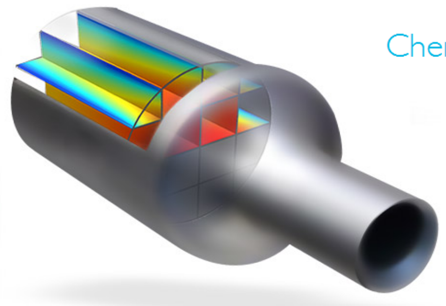
Top: Time progression of spatial distribution of temperature in the water calorimeter with exaggerated convection (using artificially large dose and buoyancy force).
Right: without convection, temperature profile in vessel remains relatively constant over time.

Now for the radiolysis – “heat defect”

Table 1. Model IIIR: reactions and rate constants (4 °C)

	Reactions[a]			Rate constants[b]
1	$e^-_{aq} + e^-_{aq}$	→	$H_2 + OH^- + OH^-$	3.48×10^9
2	$e^-_{aq} + H$	→	$H_2 + OH^-$	1.73×10^{10}
3	$e^-_{aq} + OH$	→	OH^-	2.38×10^{10}
4	$e^-_{aq} + H_2O_2$	→	$OH^- + OH$	8.84×10^9
5	$e^-_{aq} + O_2$	→	O_2^-	1.16×10^{10}
6	$e^-_{aq} + O_2^-$	→	$HO_2^- + OH^-$	8.48×10^9
7	$e^-_{aq} + HO_2$	→	HO_2^-	8.48×10^9
8	$H + H$	→	H_2	3.44×10^9
9	$H + OH$	→	H_2O	1.21×10^{10}
10	$H + H_2O_2$	→	$OH + H_2O$	3.18×10^7
11	$H + O_2$	→	HO_2	9.58×10^9
12	$H + HO_2$	→	H_2O_2	7.24×10^9
13	$H + O_2^-$	→	HO_2^-	7.24×10^9
14	$OH + OH$	→	H_2O_2	3.76×10^9
15	$OH + H_2$	→	$H + H_2O$	2.40×10^7
16	$OH + H_2O_2$	→	$H_2O + H_2O$	1.79×10^7
17	$OH + HO_2$	→	$H_2O + O_2$	9.08×10^9
18	$OH + O_2^-$	→	$OH^- + O_2$	7.89×10^9
19	$HO_2 + HO_2$	→	$H_2O_2 + O_2$	3.72×10^5
20	$HO_2 + O_2^-$	→	$H_2O_2 + O_2 + OH^-$	5.84×10^7
21	H_2O	→	$H^+ + OH^-$	2.22×10^{-6}
22	$H^+ + OH^-$	→	H_2O	7.23×10^{10}
23	H_2O_2	→	$H^+ + HO_2^-$	1.34×10^{-2}
24	$H^+ + HO_2^-$	→	H_2O_2	3.13×10^{10}
25	$H_2O_2 + OH^-$	→	$HO_2^- + H_2O$	7.56×10^9
26	$HO_2^- + H_2O$	→	$H_2O_2 + OH^-$	5.45×10^5
27	H	→	$e^-_{aq} + H^+$	8.83×10^{-1}
28	$e^-_{aq} + H^+$	→	H	1.88×10^{10}
29	$e^-_{aq} + H_2O$	→	$H + OH^-$	5.08×10^0
30	$H + OH^-$	→	$e^-_{aq} + H_2O$	7.77×10^6
31	OH	→	$H^+ + O^-$	1.34×10^{-2}
32	$H^+ + O^-$	→	OH	3.13×10^{10}
33	$OH + OH^-$	→	$O^- + H_2O$	7.56×10^9
34	$O^- + H_2O$	→	$OH^- + OH$	5.45×10^5
35	HO_2	→	$O_2^- + H^+$	4.21×10^5
36	$O_2^- + H^+$	→	HO_2	3.13×10^{10}
37	$HO_2 + OH^-$	→	$O_2^- + H_2O$	7.91×10^9
38	$O_2^- + H_2O$	→	$HO_2 + OH^-$	1.94×10^{-2}
39	$O^- + H_2$	→	$H + OH^-$	7.95×10^7
40	$O^- + H_2O_2$	→	$O_2^- + H_2O$	3.44×10^8
41	$OH + HO_2^-$	→	$OH^- + HO_2$	5.17×10^9
42	$OH + O^-$	→	HO_2^-	6.02×10^9
43	$e^-_{aq} + HO_2^-$	→	$O^- + OH^-$	2.19×10^9
44	$e^-_{aq} + O^-$	→	$OH^- + OH^-$	1.82×10^{10}
45	$O^- + O_2$	→	O_3^-	2.63×10^9
46	O_3^-	→	$O_2 + O^-$	6.70×10^2
47	$O^- + HO_2^-$	→	$O_2^- + OH^-$	2.84×10^8
48	$O^- + O_3^-$	→	$OH^- + OH^- + O_2$	4.26×10^8
49	$HO_2 + H_2O_2$	→	$OH + H_2O + O_2$	2.90×10^{-1}
50	$O_2^- + H_2O_2$	→	$OH^- + OH + O_2$	9.30×10^{-2}

N.V. Klassen and Carl K. Ross, J. Res. Natl. Inst. Stand. Techol. **107**, 171-178 (2002).



Chemical Reaction Engineering Module

The Chemical Reaction Engineering Module is optimized for the modeling of reactors, filtration and separation units, and other equipment common in the chemical and similar industries. It is specifically designed to easily couple fluid flow and mass and energy transport to chemical reaction kinetics. Firstly, the Chemical Reaction Engineering Module uses reaction formulas to create models of reacting systems. It can then solve the material and energy balances for such systems, including the reaction kinetics, where the composition and temperature vary with time, space, or both.

The Chemical Reaction Engineering Module melds seamlessly with the power of COMSOL Multiphysics for coupled as well as equation-based modeling. This allows for the inclusion of arbitrary expressions, functions, and source terms in the material property, transport, and reaction kinetic equations. You also have access to a variety of thermodynamic and physical property data through the

System inputs:

- Reaction equations and rate constants
- Heats of formation for 13 species
- G values – production rates for subset of 13 due to radiolysis by x-rays (mol/J).
- (Spatial variations neglected on first pass.)

Heat defect studies

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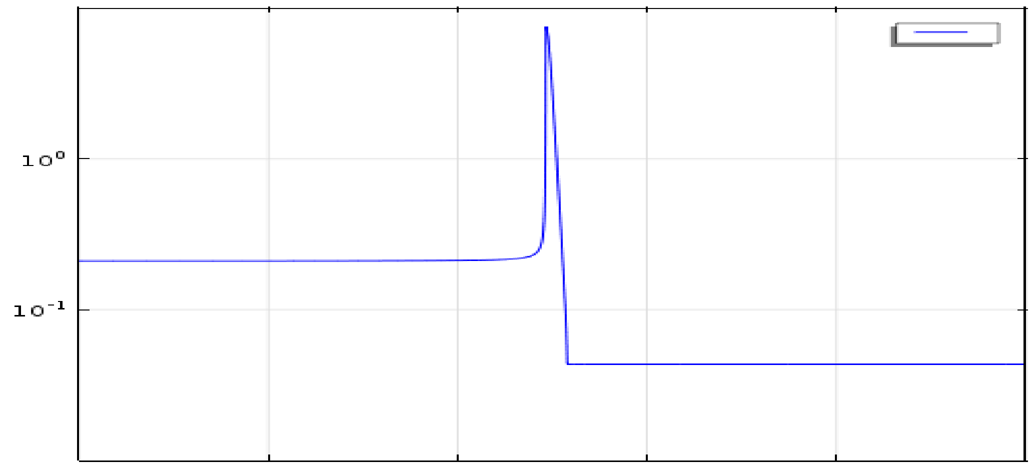

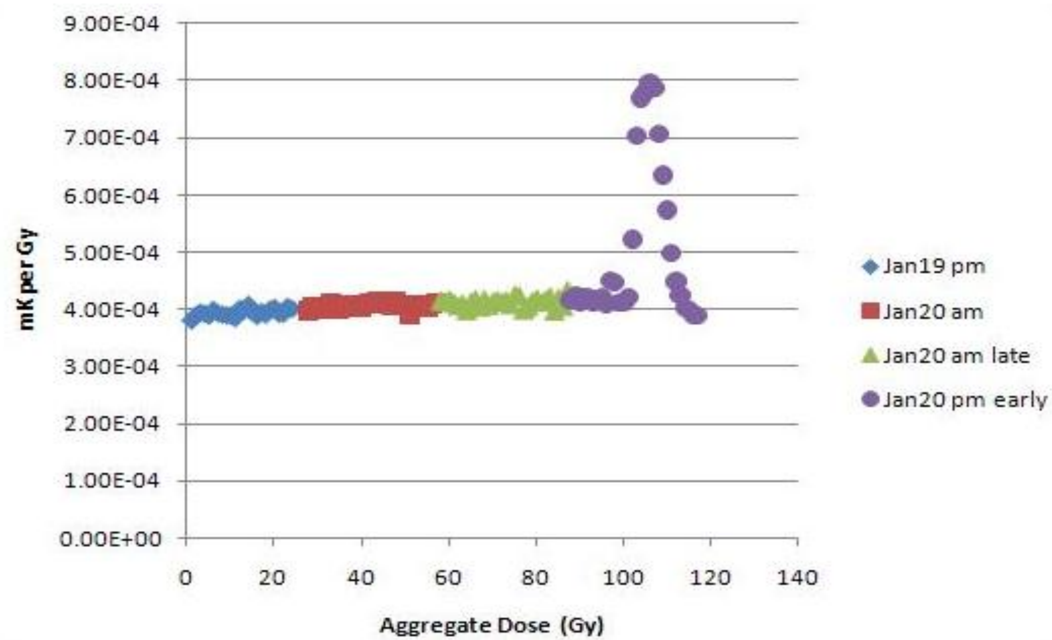

Conclusions

Heat Transfer Module – enabled us to separately quantify convection (from conduction) in heat transfer corrections.

- *Threshold for convection appears to be beyond domain of experimental conditions.*

Chemical Reaction Engineering Module – enabled us to quickly “sandbox” a complex reaction model and get qualitative agreement with experiment.

- *Threshold for accumulated dose beyond which heat defect is (possibly) negligible being further studied.*